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RADIOCARBON ANALYSIS OF METHANE AT THE NERC RADIOCARBON FACILITY (EAST KILBRIDE)

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ABSTRACT

Methane is the second most important anthropogenically-produced greenhouse gas, and radiocarbon analysis is extremely valuable in identifying its age and source in the environment. At the NERC Radiocarbon Facility (East Kilbride, UK) we have developed expertise in analysis of methane radiocarbon concentration and methodological approaches to field sampling over the past twenty years. This has opened a wide range of applications, which have mainly focussed on: i) the age and source of methane emitted by peatlands and organic soils (e.g. to quantify the release of ancient carbon), ii) the source of aquatic emissions of methane, and iii) the age of methane generated by amenity and illegal landfill. Many of these scientifically important applications involve challenging sampling and measurement considerations, which our development programme has continually aimed to overcome. Here, we describe our current methods, and recent improvements to aid field collection of samples in remote locations. We present the results of tests which i) show the effectiveness of our methods to remove contaminants, especially CO_2, ii) quantify the radiocarbon background contribution, and iii) demonstrate the reliability of metal gas storage canisters for sample storage.

INTRODUCTION

Methane (CH_4) is a greenhouse gas with a global warming potential around twenty or more times that of carbon dioxide (CO_2) and its concentration in the atmosphere is increasing (Turner et al. 2017). Despite the major global sources of CH_4 being now largely identified, their relative contributions to the overall budget remain highly uncertain (Kirschke et al. 2013). Radiocarbon (^{14}C) analysis offers a way to address this problem, by providing unique information on the age and source of CH_4. For example, CH_4-derived from contemporary biogenic activity contains modern ^{14}C signatures, while detectable ^{14}C is absent from fossil CH_4 (i.e. indistinguishable from background) due to its great age. Thus, the concentration of ^{14}C in CH_4 has been used to determine the biogas-fraction in domestic gas supplies (e.g. Palonen et al. 2017). Moreover, measurement of the ^{14}C content of CH_4 has provided powerful evidence on the contribution of ancient CH_4 to contemporary emissions in peatland (Cooper et al. 2017) and marine environments (Sparrow et al. 2018), giving valuable insights into how these ecosystems are responding to climate change.

At the Natural Environment Research Council (NERC) Radiocarbon Facility (East Kilbride, UK) we have been developing techniques for the radiocarbon analysis of CH_4 for over twenty years. Methods for the field collection of samples have been established for aquatic CH_4 (Garnett et al. 2016; Dean et al. 2017), together with CH_4 in the surface emissions (Garnett et al. 2012) and sub-surface layers (Garnett et al. 2011) of peatlands. Sample CH_4 concentrations can vary widely, from less than 100

ppm to tens of % CH_4. Laboratory processing of samples begins with the purification of the gas samples to isolate the CH_4 from carbon-containing contaminants; these are almost exclusively carbon dioxide in the typical sample types that we process. This step was initially undertaken using a purely cryogenic approach (Clymo and Bryant 2008) but is now achieved using soda lime (which reacts to remove CO_2) and/or zeolite molecular sieve (the zeolite adsorbs the CO_2, which can be recovered later for analysis if required; Garnett et al. 2011).

Radiocarbon analysis of CH_4 in remote locations is still challenging, particularly when the CH_4 occurs at low concentrations, and therefore requires the sampling of many litres of air to meet sample size requirements (typically a minimum of 0.5 mg CH_4-C or 1 ml CH_4 is required). Samples can be contained inside gas sampling bags (e.g. SKC foil gas bag, SKC Ltd), however, these are generally only recommended for single use, are considered unsuitable for long-term storage (the manufacturer recommends analysing the samples within 48 hrs), and are not suitable for air freight in non-pressurised cargo cabins (SKC literature, SKC Ltd). Whereas CO_2 samples can be conveniently concentrated into a small volume of adsorbent such as zeolite molecular sieve (Garnett and Murray 2013), an equivalent approach does not exist for CH_4 (Palonen et al. 2017). Molecular sieves can efficiently adsorb CH_4 when chilled (Kessler and Reeburgh 2005), but the requirement of cryogenic coolants (e.g. liquid nitrogen) means that such an approach is unlikely to be suitable for sampling in remote locations (the chilled molecular sieve also traps more abundant gases such as nitrogen, and so can be potentially hazardous; Kessler and Reeburgh 2005). A promising method is the field-conversion of sample CH_4 to carbon dioxide and subsequent trapping of the CH_4-derived CO_2 on molecular sieve (Cooper et al. 2017; Palonen et al. 2017), although the power-demands to operate a furnace in remote field locations is likely to be a limitation.

Another approach for the collection of CH_4 samples is the use of metal air sampling canisters (large glass flasks can also be used but are more fragile and vulnerable to breakage). Although more expensive than gas sample bags, they should provide considerable advantages for sampling in remote locations due to greater robustness and sample storage performance. Here, we describe our latest methods for processing CH_4 samples for radiocarbon analysis which have been adapted to facilitate the use of metal gas canisters. We also report the results of tests used to verify the methods and canisters.

METHODS

Description of sample processing methods

Prior to use, storage vessels are cleaned by evacuating to $<1 \times 10^{-3}$ mB, flooded with high purity nitrogen gas (purity 99.999 %, BOC, UK), and evacuated again to $<1 \times 10^{-3}$ mB (Edwards RV5 and RV12 Rotary Vane vacuum pumps fitted with foreline traps to prevent back migration of oil mist). Sampling is performed by using the canister's vacuum to draw in sample gas via a hydrophobic filter (50 mm diameter PTFE membrane syringe filter, Corning, Germany) which prevents the entry of particulates and liquid water.

On return to the laboratory, sample CH_4 is recovered (as CH_4-derived CO_2) by connecting the canister to a vacuum rig (Figure 1) and first evacuating the line up to the valve on the gas canister. The rig is constructed from stainless steel vacuum tubing (6 mm o/d) and Swagelok fittings (Swagelok, USA). After isolating the vacuum pump, sample gas is introduced to the rig through a column containing

self-indicating soda lime (Fisher Scientific, UK) which removes CO_2. The gas then passes through a column of Type 13X zeolite molecular sieve (3-4 g, 1.6 mm pellets, Sigma-Aldrich, UK) which has been prepared by heating (500 ^oC) and purging with nitrogen (Garnett and Murray 2013). The molecular sieve provides a secondary trap for traces of CO_2 that may have been missed by the soda lime and removes water including that generated from the CO_2 reacting with the soda lime. Connections between the canister, soda lime and molecular sieve columns are made using stainless steel and Iso-Versinic tubing (Figure 1; Saint-Gobain, France). Sample CH_4 is then combusted to CO_2 by reacting with a platinum catalyst (~8 g platinized alumina beads contained in a quartz glass tube; Johnson Mathey Chemicals, UK) heated to 950 ^oC (i.e. maximum temperature of the furnace), dried using a slush trap (dry ice with industrial methylated spirits; -78 ^oC), and the CH_4-derived CO_2 cryogenically recovered in two liquid nitrogen traps (-196 ^oC). The vacuum pump is used to draw sample gas from the canister through the rig (slowly at first, by only partially opening the valve to the pump), until a vacuum of ~1 x 10^{-2} mB has been achieved. The recovered CO_2 is then transferred to a volume-calibrated cold finger connected to a pressure transducer and the CO_2 volume determined. In between samples the heated platinum catalyst is regenerated by flooding with high purity oxygen and then evacuated.

Tests performed to verify the reliability of the sample processing methods

Our CH_4 processing methods have previously been verified for samples that maintained a constant atmospheric pressure during processing (i.e. when supplied in foil gas bags; e.g. Garnett et al. 2012), or for relatively small gas volumes in glass flasks (~215 mL, Garnett et al. 2011). We therefore first tested whether the same rig design was suitable when processing gas volumes of greater than 2 L by replacing the gas bags with a 2.2 L glass vessel that was required to be evacuated during the processing of a sample. These initial tests were used to inform on whether the laboratory methods were likely to be reliable for 6 L metal canisters, prior to their procurement. For these tests, we pumped 8 L of outside air into a 10 L foil gas bag and used a gas-tight syringe to add a further ~100 ml of CO_2 (Air Products Ltd, UK) with a ^{14}C content of ~70 %modern (see Stuiver and Polach 1977 for the definition of %modern), and ~20 ml of "fossil" CH_4 (BOC Ltd, UK) which we use as an internal laboratory background standard. The gas mixture was then transferred in aliquots into an evacuated 2.2 L glass flask and processed on the rig as described above. Three 2.2 L aliquots were processed from the same gas mixture in the 10 L bag. We chose to use atmospheric air for these tests since it would more closely simulate samples (e.g. containing water vapour), and because the relatively high CH_4 standard concentration would mean that atmospheric CH_4 would be a small fraction of the total CH_4, which we corrected for using:

$$Ci_{corr} = ((Ci_{meas} \times V_{meas}) - (Ci_{atmos} \times V_{atmos})) / (V_{meas} - V_{atmos}) \qquad \textit{(Equation 1)}$$

Where *Ci* is the isotopic concentration (^{14}C or $\delta^{13}C$) of the atmosphere ($_{atmos}$), measured sample ($_{meas}$) and sample corrected for atmospheric CH_4 ($_{corr}$). V_{meas} is the total volume of CH_4-derived CO_2 recovered, and V_{atmos} the volume of atmospheric CH_4 in the sample which is calculated from the volume of the sampling vessel and assuming for atmospheric CH_4 a concentration of 1.9 ppm, a ^{14}C content of 130 %modern and a $\delta^{13}C$ of -47 ‰ (Lassey et al. 2007).

We next tested our methods for analysing CH_4 samples that are smaller than the minimum sample size of 0.5 mg C; this is currently the lower limit for routine samples at the NERC Radiocarbon Facility (East Kilbride). To avoid atmospheric CH_4, we created synthetic air by mixing 7 L of nitrogen gas (purity 99.999 %, BOC, UK), 1 L of oxygen (purity 99.9995%, BOC, UK) and ~100 ml of CO_2 with a ^{14}C content of ~70 %modern (Air Products Ltd, UK), to which we added ~2 ml of our "fossil" CH_4 (BOC Ltd, UK) internal laboratory standard. We again transferred aliquots of this bulk gas into a 2.2 L glass flask and recovered the CH_4 component using the same methods as described above.

To test the 6 L metal canisters (6 L Silonite Canister, Entech Instruments, USA) we performed an identical test to the previous one except with slightly more CH_4 to ensure that the recovered sample was routine-sized (i.e. 6 L of gas was transferred into the canister from a foil gas bag containing 7 L nitrogen, 1 L oxygen, 100 ml CO_2 and ~4 ml ^{14}C-dead CH_4). We assessed the storage performance of the 6 L metal canisters by preparing two identical standard gases containing ~5 L N_2 and ~1 L O_2 to which ~4-5 ml of ^{14}C-dead CH_4 was directly injected into the canister using a gas-tight syringe. One sample was processed immediately, while the second was left for three months before processing (the longest amount of time that we expect to use the canisters for sample storage).

A final test was undertaken to assess the reliability of the 6 L canisters for processing non-background CH_4 samples. Relatively ^{14}C-enriched CH_4 was obtained from a biogas plant (GBM, Bristol, UK) and stored in a pressurised cylinder. One aliquot of this gas was analysed directly through the rig (after being injected into a 1 L bag of O_2) and provided the reference value. A second aliquot was injected into a 6 L metal canister prefilled with ~5 L N_2 and ~1 L O_2 and then processed as previously.

The tests described above were used to check the reliability of the new storage and sample purification steps, in addition to the subsequent stages of routine sample processing (e.g. graphitisation). We also analysed several CH_4 standards which served as blanks to test the sample processing under optimised conditions i.e. CO_2-free and with minimal storage. These standards, which we term "CH_4 blanks" were a mix of ~5 ml ^{14}C-dead CH_4 in ~1 L high purity O_2 that had been freshly prepared in a 1 L foil gas bag prior to being processed by directly connecting the bag to the rig.

After passing through the rig, one aliquot of CH_4-derived CO_2 from each of the routine sized (>0.5 mg C) samples was used for determining $\delta^{13}C$ relative to the Vienna PDB international standard using isotope ratio mass spectrometry (IRMS; Thermo-Fisher Delta V, Germany). For all samples, an aliquot of CO_2 was converted to graphite using Fe-Zn reduction (Slota et al. 1987) and measured using accelerator mass spectrometry (AMS). Routine-sized samples were analysed at the Scottish Universities Environmental Research Centre AMS Facility (East Kilbride, UK) and smaller samples were measured at the Keck AMS Facility (UC Irvine, USA). Following convention (Stuiver and Polach 1977), radiocarbon measurements were normalised to $\delta^{13}C$ of -25 ‰ and expressed as %modern, and conventional radiocarbon ages (years BP, where 0 BP = AD 1950). A laboratory background correction of 0.17 %modern was applied to the biogas ^{14}C results, based on the long-term record for ^{14}C-dead CH_4 standards processed in the lab. No background correction was applied to the other results. Isotope mass balance was used to calculate the mass of modern carbon (100 %modern) required to account for the deviation in ^{14}C concentrations above zero in the samples of ^{14}C-dead CH_4.

RESULTS

The radiocarbon concentration of routine-sized samples of ^{14}C dead CH_4 recovered from 2.2 L of atmospheric air augmented with 25 ml of ~70% modern CO_2 ranged from 0.26±0.01 to 0.27±0.01 %modern (Table 1). Correcting for atmospheric CH_4 using isotope mass balance (Equation 1) reduced the ^{14}C contents to 0.12±0.01 to 0.14±0.01 %modern (52,615±195 to 53,851±207 BP). The %modern values for these three standards were only slightly greater than for the similarly sized CH_4 blank processed at the same time (Table 1).

There was a greater range in ^{14}C content for the small CH_4 samples recovered from synthetic air, extending from 0.29±0.01 to 0.74±0.02 %modern (47,020 to 39,440 BP; Table 2). Although the sample with the smallest volume had the highest ^{14}C content, the results did not suggest a strong dependency of ^{14}C content on sample size. Furthermore, when expressed in terms of modern carbon contamination the small samples (0.8 to 2.0 µg C) had a lower contamination compared to the routine-sized samples (2.7-3.4 µg C).

The three samples of ^{14}C-dead CH_4 used for testing the 6 L metal canister all gave comparable results (0.11±0.01 to 0.16±0.01 %modern; Table 3) and in terms of both ^{14}C content and mass of modern carbon contamination were similar to the 2.2 L glass flask (Table 1; after the latter had been corrected for atmospheric CH_4). Although the CH_4 stored for 3 months in the 6 L metal canister had a slightly higher ^{14}C content (0.16±0.01 %modern) than the reference standard that had been processed immediately (0.13±0.01 %modern), the results overlapped at <2 σ analytical uncertainty (Table 3). The biogas CH_4 had a ^{14}C content that was just under 100 %modern, with the reference gas and sample processed from the canister providing identical radiocarbon concentrations (i.e. within 1 σ; Table 3).

DISCUSSION

The routine-sized (>0.5 mg C) CH_4 standards processed using our latest procedures all produced very good ^{14}C results, with background-uncorrected radiocarbon ages more than 50,000 BP (Tables 1 and 3). Importantly, the %modern values for these routine-sized samples covered a narrow range from 0.11±0.01 to 0.16±0.01 %modern, demonstrating a small (1.9-3.8 µg C) but reproducible contamination that can be reliably accounted for using routine ^{14}C background correction. Indeed, there was very little ^{14}C difference, if any, between routine-sized samples collected in glass flasks or metal canisters, suggesting the vessels performed equally well (although we note that the relative fragility of the glass flask makes it less suitable for fieldwork). Similarly, air mixtures containing additional 70 %modern CO_2 were not ^{14}C-enriched showing that the soda lime and molecular sieve traps are very effective at removing potentially contaminating CO_2 (Tables 1 and 3). Similar ^{14}C concentrations have been reported by previous researchers for ^{14}C-dead CH_4 samples. For example, Sparrow and Kessler (2017) reported a ^{14}C blank of 0.23±0.07 %modern (0.24 µg C) for their CH_4 preparation system, and Elder et al. (2018) quantified modern ^{14}C blank in their CH_4 processing apparatus to be ~1.5-2.5 µg C (which compares to 0.5-3.8 µg C for our samples). Palonen et al. (2017) measured a ^{14}C content of 0.06±0.07 %modern for natural gas (after applying a background correction of 0.4±0.1 %modern).

The CH_4 sample recovered from the metal canister after 3 months storage was slightly higher in ^{14}C content compared to an identical sample processed immediately. This might suggest limitations on

the use of these canisters for the storage of CH_4 samples. However, the ^{14}C result for the stored CH_4 sample differed by <2 σ compared to the control canister and was similar in ^{14}C content compared to the routine-sized glass flask samples. We therefore consider there to be insufficient evidence to suggest that the canister is unsuitable for long-term storage of CH_4 samples, and indeed, given that most of the CH_4 samples that we process are relatively young (<5000 years BP), we conclude that the storage performance of the canister is acceptable for our purposes.

The ^{14}C %modern values of the small-sized samples were higher compared to the routine-sized samples (Table 2), indicating that further improvements are necessary to reliably date sub-millilitre CH_4 samples that are close to background. However, we note that the mass of carbon inferred from the ^{14}C measurements is lower in the small-samples compared to the routine-sized. That the ^{14}C content of the CH_4 blank was significantly lower than the other small samples might suggest incomplete removal of the 70 %modern CO_2 that was added to the latter. However, it could alternatively be derived from impurities in the N_2 that was present in the synthetic air but not the CH_4 blank.

While the results presented here support the reliability of our methods for accurate measurement of CH_4, several limitations need to be acknowledged. Firstly, though our methods reliably remove CO_2, which we believe is by far the most likely contaminant of our sample types, other contaminants could occur, albeit in far smaller quantities (such as carbon monoxide and non-CH_4 hydrocarbons e.g. ethane). It is possible that the molecular sieve used in our processing line may remove some of these contaminants if present (e.g. Rege et al. 2000). Alternatively, if the contaminants have a similar ^{14}C content to the sample CH_4 (e.g. due to a common source) then small traces of them will not significantly change the ^{14}C results. Nevertheless, in cases where contaminants are of concern, steps should be taken to remove them. For example, carbon monoxide can be removed using a metal catalyst (Polonen et al. 2017) or by oxidation followed by adsorption on molecular sieve (Sparrow and Kessler 2017); non-CH_4 hydrocarbons can be removed in liquid nitrogen cooled traps at 223 torr (Sparrow and Kessler 2017).

Additionally, in our trials we predominantly used ^{14}C-dead CH_4 to assess the reliability of our methods because it is readily available and being ^{14}C-dead provides a sensitive test for non-^{14}C dead contaminants which we consider are most likely (e.g. atmospheric CO_2 and CH_4). To detect ^{14}C-dead or depleted contamination would require a relatively ^{14}C-enriched CH_4 standard. Unfortunately, to our knowledge an equivalent non-background $^{14}CH_4$ standard is not available (see also Pack et al. 2015), and hence while the CH_4 biogas that we used in our tests provided identical results for canister and non-canister processed samples, they do not provide independent verification of the true ^{14}C content of this gas. However, using the same rig and almost identical sample processing methods we have previously demonstrated reliability of our methods; CH_4 produced from decomposing leaves in a small anaerobic digester had the same ^{14}C content as atmospheric CO_2 in the year of collection (Garnett et al. 2016).

In our suite of tests, the $\delta^{13}C$ values that we obtained for our internal laboratory CH_4 standard ranged from -46.2±0.3 to -41.5±0.3 ‰ for IRMS measurements. These inconsistent $\delta^{13}C$ values are unlikely to be a result of contamination, otherwise we would not have achieved such reproducible and low %modern results for the same standards. Instead, isotopic fractionation seems a more likely explanation. This could have been caused by incomplete combustion of CH_4 during sample processing, although we think that this explanation is unlikely. Instead, we believe that fractionation probably occurred through not isotopically equilibrating the gas mixtures during their transfer from

the 10 L foil gas bag to the glass flask. Hence, there was a pattern whereby the first two aliquots of the standard gases were relatively ^{13}C-depleted, and the residual gas used for the third aliquot was ^{13}C-enriched (Tables 1 and 2). Which of the above explanations is correct could have been resolved with accurate measurement of CH_4 yield. Unfortunately, we were unable to obtain accurate yields because: a. preparation of the standard gases using the syringe did not allow us to accurately determine the volume of gas used, and b. our CH_4 standard gas was not 100 % pure (the syringe was cleaned by flushing with high purity oxygen and small amounts of this were progressively introduced to the CH_4 standard from "dead space" within the syringe). Nevertheless, fractionation due to either process would not impact the ^{14}C measurements, since these were normalised according to convention, and therefore corrected for fractionation (Stuiver and Polach, 1977). Our future development programme will aim to identify and eliminate the cause of this isotopic fractionation.

In conclusion, the results presented here demonstrate the reliability of our methods for measuring the radiocarbon content of CH_4. Tests on the 6 L metal canisters support their suitability for collection and storage of CH_4 samples, which will be especially beneficial for sample collection in remote locations. Future development will focus on further improving the quality of results with a focus on smaller sample sizes.

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Table 1 Results for routine-sized CH_4 samples in a glass flask. Composition of the gas mixture was approximately 2.2 L outside air, 4-5 ml ^{14}C-dead CH_4 and 25 ml of 70 %modern CO_2. ^{14}C results presented before and after correcting for atmospheric CH_4 ($\delta^{13}C$ results were unchanged following this correction).

Publication code (SUERC-)	Gas mixture	CH_4-derived CO_2 recovered (ml)	IRMS $\delta^{13}C_{VPDB}$ ±0.3 ‰	^{14}C content (%modern ±1 σ)	Air-corrected ^{14}C content (%modern ±1 σ)	Conventional ^{14}C age (BP± 1 σ)	Background contribution (µg C)
75784	Air+ CH_4/CO_2	4.50	-45.9	0.27±0.01	0.14±0.01	52,615±195	3.4
75785	Air+ CH_4/CO_2	4.16	-46.2	0.26±0.01	0.12±0.01	53,851±207	2.7
75786	Air+ CH_4/CO_2	4.66	-43.6	0.26±0.01	0.14±0.01	52,939±193	3.4
75783	CH_4 blank	5.18	-43.2	0.11±0.01	n/a	54,580±438	3.1

334 **Table 2** Results for small-sized CH_4 samples in a 2.2 L glass flask. Synthetic air (high purity N_2 and O_2)
335 was used to which was added approximately 0.5 ml ^{14}C-dead CH_4 and 25 ml of 70%modern CO_2. NB.
336 $\delta^{13}C$ was measured by AMS on sample prepared to graphite and may not be representative of the
337 recovered CH_4-derived CO_2.

338

Publication code (UCIAMS-)	Gas mixture	CH_4-derived CO_2 recovered (ml)	AMS $\delta^{13}C_{VPDB}$ ‰	^{14}C content (%modern ±1 σ)	Conventional ^{14}C age (BP ±1 σ)	Background contribution (µg C)
192871	Synth air +CH_4/CO_2	0.63	-36.1	0.41±0.01	44,200±220	1.4
192862	Synth air +CH_4/CO_2	0.51	-37.1	0.74±0.02	39,440±240	2.0
192856	Synth air +CH_4/CO_2	0.54	-31.1	0.29±0.01	47,020±220	0.8
192857	CH_4 blank	0.43	-32.0	0.23±0.01	48,840±260	0.5

339

340 **Table 3** Testing 6 L metal canisters for collection and storage of CH_4 samples. Synthetic air (high
341 purity N_2 and O_2) was used to test CO_2 removal and storage performance of the metal canisters (by
342 adding ^{14}C-dead CH_4 and 70 %modern CO_2). Two samples of relatively ^{14}C-enriched CH_4 (GBM CH_4)
343 were also analysed, with and without the use of the canister.

344

Publication code (SUERC-)	Gas mixture	CH_4-derived CO_2 recovered (ml)	IRMS $\delta^{13}C_{VPDB}$ ±0.3 ‰	^{14}C content (%modern ±1 σ)	Conventional ^{14}C age (BP ± 1 σ)	Background contribution (µg C)
77589	Synth air +CH_4/CO_2	3.29	-41.5	0.11±0.01	54,652±370	1.9
76521	Synth air +CH_4	4.84	-43.2	0.13±0.01	53,321±479	3.4
77588	Synth air +CH_4 storage test	4.39	-43.6	0.16±0.01	51,714±333	3.8
79894	GBM CH_4 (canister)	3.92	-56.7	98.67±0.45	107±36	-
79895	GBM CH_4 (reference)	1.66	-56.6	97.82±0.44	177±36	-

345

Figure cations

Figure 1 Schematic illustrating the processing of CH_4 samples on a vacuum system. LN = liquid nitrogen, IMS = industrial methylated spirits.